[CONTRIBUTION FROM MULTIPLE FELLOWSHIPS ON CATALYSIS[1] AND TAR SYNTHETICS,[2] MELLON INSTITUTE]

Butadiene from Ethanol. Reaction Mechanism

BY H. E. JONES, E. E. STAHLY AND B. B. CORSON

The manufacture of butadiene from ethanol by the American two-step process developed by Carbide and Carbon Chemicals Corporation[3,4] and operated by that organization and by Koppers Company, Inc., comprised (1) dehydrogenation of ethanol to acetaldehyde followed by (2) catalysis of acetaldehyde–ethanol to produce butadiene. This paper discusses the mechanism of the second step, in which a mixture of approximately 69 wt. % of ethanol, 24 wt. % of acetaldehyde and 7 wt. % of water was passed over a 2% Ta_2O_5–98% SiO_2 catalyst at 350° and 0.4 liquid hourly space velocity (l.h.s.v.). Mechanistic evidence was obtained from rate measurements and from the behavior of various feed mixtures.

The importance of crotonaldehyde as intermediate[4] was confirmed. The primary function of the silica component of the catalyst was the condensation of acetaldehyde to crotonaldehyde, whereas that of the tantala promoter was the catalysis of the deoxygenation of crotonaldehyde by the hydrogen donor ethanol. This is a reversal of the roles assigned by Quattlebaum, Toussaint and Dunn.[4] Crotyl alcohol and acetaldol, perhaps transitory intermediates, were not rate controlling. Both crotonaldehyde and crotyl alcohol were present in the crude catalyzate, but acetaldol was not detectable.

The odor of the liquid portion of the catalyzate furnished qualitative evidence of the presence of crotonaldehyde. The latter[5] was separated by distillation, as well as crotyl alcohol.[6] Crotyl alcohol was subsequently isolated in considerable amount from plant by-product *n*-butanol and shown to constitute about 0.8% of the "by-product oil."

Kinetic study indicated that the rate controlling process at atmospheric pressure was a second order condensation of acetaldehyde, whereas at pressures of 4–30 atmospheres the rate of consumption of acetaldehyde was of first order.

The behavior of various feed mixtures when passed over the catalyst indicated that diethyl acetal, vinyl ethyl ether, diethyl ether, *n*-butanol, *n*-butanediols, *n*-butyraldehyde, ethylene, acetylene and tetrahydrofuran were not major intermediates. In general, as would be expected, feed mixtures capable of producing ethanol and acetaldehyde (or crotonaldehyde) *in situ*, yielded butadiene. Crotyl alcohol mixed with a small amount of crotonaldehyde produced a 60% per pass yield of butadiene when passed over the catalyst, crotonaldehyde being continuously regenerated from crotyl alcohol by the deoxygenation reaction which produced butadiene (mechanism E).

Experimental

Materials.—Ethanol, acetaldehyde and crotonaldehyde were of reagent grade. Crotyl alcohol (b. p. 117–119°, $n^{20}{}_D$ 1.4255, $d^{20}{}_4$ 0.855, 96% pure by bromine number, characterized as α-naphthylurethan, m. p. 91–93°) was prepared by the reduction of crotonaldehyde by aluminum isopropoxide. The various other feed materials were purchased, all samples being analyzed or characterized before use; if the purity was not 95% or better, the material was purified.

Commercial catalyst (2% Ta_2O_5–98% SiO_2) was obtained from the Rubber Reserve Company. Silica gel of the type employed in the preparation of the above catalyst was obtained from the Davison Chemical Company, its specifications being those of the Rubber Reserve acceptance test.

Apparatus and Procedure.—Two types of equipment were employed, the Koppers reactor[7] charged with 125 cc. of catalyst, and a single tube of the multiple tester[8] charged with 20 cc. of catalyst.

Catalyzate from the larger reactor was condensed by Dry Ice and distilled into three fractions: (1) b. p. below 13°, (2) b. p. 13–30° and (3) b. p. 30–95°, which fractions were analyzed, respectively, for (1) butadiene and acetaldehyde, (2) acetaldehyde and (3) acetaldehyde, acetal and ethanol. Operation at 350° and 0.4 l. h. s. v. (6.6 seconds contact time) with commercial feed (2.75 moles of ethanol per mole of acetaldehyde) and commercial catalyst (2% Ta_2O_5–98% SiO_2) gave a 36% per pass yield of butadiene and a 64% ultimate yield (standard deviations 2.5 and 1.6%, respectively). This ultimate yield duplicated commercial practice.

Catalyzate from the smaller reactor was processed by extractive distillation[9] to separate gaseous from liquid products. The gas was collected over aqueous sodium sulfate and analyzed for butadiene by the Koppers-Hinckley method[10]; the liquid catalyzate (bottoms from extractive distillation—by-products and unreacted feed) was not analyzed, being too small for significant ultimate yield data. The per pass butadiene yield averaged 35% (with commercial feed and commercial catalyst) which was in good agreement with the 36% value obtained with the larger equipment.

Mechanisms

Many of the mechanisms[11] which have been hypothesized to explain the formation of butadiene are characterized by lack of evidence. Mechanisms involving the formation and deoxygenation of crotonaldehyde (mechanisms B, B_1 and D) were indicated by the present study and had been previously derived by Quattlebaum, Toussaint and

---

[1] Reconstruction Finance Corporation, Office of Rubber Reserve, Washington, D. C.

[2] Koppers Company, Inc., Pittsburgh, Pa.

[3] Toussaint, Dunn and Jackson, *Ind. Eng. Chem.*, **39**, 120 (1947).

[4] Quattlebaum, Toussaint and Dunn, THIS JOURNAL, **69**, 593 (1947).

[5] 2,4-Dinitrophenylhydrazone, m. p. and mixed m. p. 189–191°.

[6] Identified by hydrogenation to *n*-butanol.

[7] Corson, Stahly, Jones and Bishop, *Ind. Eng. Chem.*, in press.

[8] Whitlock, Haddad and Stahly, *Ind. Eng. Chem., Anal. Ed.*, **19**, 767 (1947).

[9] Hinckley and Sheppard, *ibid.*, **19**, 771 (1947).

[10] Rubber Reserve method L. M. 2.1.1.7 (or 2.1.1.9.); Shepherd, Thomas, Schumann and Diebler, *J. Research, Natl. Bur. Standards*, **39**, 435 (1947).

[11] Egloff and Hulla, *Chem. Revs.*, **36**, 63 (1945).

Dunn[4] from their study of the Ostromislensky reaction.[12]

(A) $CH_3CHO + C_2H_5OH \longrightarrow CH_2{=}CHCH{=}CH_2 + 2H_2O$

(B) $2CH_3CHO \longrightarrow CH_3CH{=}CHCHO + H_2O$

(B₁) $2CH_3CHO \longrightarrow CH_3CHOHCH_2CHO \longrightarrow CH_3CH{=}CHCHO + H_2O$

(C) $CH_3CH{=}CHCHO + C_2H_5OH \longrightarrow CH_3CHO + CH_3CH{=}CHCH_2OH \longrightarrow CH_2{=}CHCH{=}CH_2 + H_2O$

(D) $CH_3CH{=}CHCHO + C_2H_5OH \longrightarrow CH_3CHO + CH_2{=}CHCH{=}CH_2 + H_2O$

(D₁) $CH_3CH{=}CHCHO + RH_2$ (H donor other than ethanol) $\longrightarrow CH_2{=}CHCH{=}CH_2 + R + H_2O$

(E) $CH_3CH{=}CHCHO + CH_3CH{=}CHCH_2OH \longrightarrow CH_2{=}CHCH{=}CH_2 + CH_3CH{=}CHCHO + H_2O$

(F) $CH_3CHOHCH_2CHO + C_2H_5OH \longrightarrow CH_3CHO + CH_3CHOHCH_2CH_2OH \longrightarrow CH_2{=}CHCH{=}CH_2 + 2H_2O$

(G) $2C_2H_5OH \longrightarrow CH_3CH_2CH_2CH_2OH + H_2O$

(G₁) $CH_3CH_2CH_2CH_2OH \longrightarrow H_2O + CH_3CH_2CH{=}CH_2 \longrightarrow CH_2{=}CHCH{=}CH_2 + H_2$

(G₂) $CH_3CH_2CH_2CH_2OH \longrightarrow H_2 + CH_3CH{=}CHCH_2OH \longrightarrow CH_2{=}CHCH{=}CH_2 + H_2O$

(G₃) $CH_3CH_2CH_2CH_2OH \longrightarrow H_2 + CH_3CH_2CH_2CHO \longrightarrow CH_3CH{=}CHCHO + H_2$

(G₄) $CH_3CH_2CH_2CH_2OH \longrightarrow CH_2{=}CHCH{=}CH_2 + H_2 + H_2O$

(H) $CH_3CHO + C_2H_5OH \longrightarrow CH_3CHOH(OC_2H_5)$

(H₁) $CH_3CHOH(OC_2H_5) \longrightarrow H_2O + CH_2{=}CH(OC_2H_5)$

(H₂) $CH_2{=}CH(OC_2H_5) + CH_2{=}CH_2 \longrightarrow CH_2{=}CHCH{=}CH_2 + C_2H_5OH$

(H₃) $CH_3CHOH(OC_2H_5) \longrightarrow CH_3CHOHCH_2CH_2OH \longrightarrow CH_2{=}CHCH{=}CH_2 + 2H_2O$

(I) $CH_3CHO + CH_2{=}CH_2 \longrightarrow CH_2{=}CHCH{=}CH_2 + H_2O$

(J) $CH_2{=}CH_2 + CH{\equiv}CH \longrightarrow CH_2{=}CHCH{=}CH_2$

(K) $-CH_2CH_2- \longleftarrow C_2H_5OH \longrightarrow -CH_2CH(OH)-$

(L) $\equiv SiOSi \equiv + C_2H_5OH \longrightarrow \equiv SiOH + \equiv SiOC_2H_5$

(M) $\equiv SiOSi \equiv + CH_2{=}CHCH{=}CH(OH) \longrightarrow \equiv SiOH + \equiv SiOCH{=}CHCH{=}CH_2$

(M₁) $\equiv SiOCH{=}CHCH{=}CH_2 + \equiv SiOC_2H_5 \longrightarrow \equiv SiOSi \equiv + CH_2{=}CHCH{=}CH_2$

The biradical mechanism (K) has little supporting evidence, and it is not necessary,[3] as originally claimed[13] for an understanding of the by-products formed. In regard to the silicon oxide complexes, although the hypothetical formation of catalyst–reactant complexes ranging from adsorption complexes to chemical compounds is a well-known concept of catalysis, it is a mechanism which in the present case takes no cognizance of the promoter action of the tantala component of the catalyst.

The mechanism of the two-step process—formation and deoxygenation of crotonaldehyde—is probably applicable to the one-step process as evidenced by the reported beneficial effect of acetaldehyde.[13,14] Minor side reactions of the two-step process become important when the conditions are intensified to approach those of the one-step process. For example, when the second step was operated at 375–400°, 0.7 l. h. s. v., with 5/1 ethanol–acetaldehyde feed mole ratio the apparent yield of butadiene based on acetaldehyde[15] surpassed 100%, which means that the original acetaldehyde content of the feed was augmented by additional acetaldehyde formed *in situ*, not only by reactions C, D and F, but probably also by reactions N, O, P, Q and R; butyraldehyde, butanol, butane and butene were detected in the catalyzate.

(N) $CH_3CH{=}CHCHO + C_2H_5OH \longrightarrow CH_3CH_2CH_2CHO + CH_3CHO$

(O) $CH_3CH_2CH_2CHO + C_2H_5OH \longrightarrow CH_3CH_2CH_2CH_2OH + CH_3CHO$

(P) $CH_3CH_2CH_2CHO + C_2H_5OH \longrightarrow CH_3CH{=}CHCH_3 + H_2O + CH_3CHO$

(Q) $CH_2{=}CHCH{=}CH_2 + 2C_2H_5OH \longrightarrow CH_3CH_2CH_2CH_3 + 2CH_3CHO$

(R) $C_2H_5OH \longrightarrow CH_3CHO + H_2$

Kinetic Studies

Effect of Feed Composition.—According to the data of Table I the general effect of increasing the acetaldehyde content of the feed was to

TABLE I

EFFECT OF FEED COMPOSITION (EXPLORATORY EXPTS).

350°, 0.4 l. h. s. v., 2% Ta_2O_5–98% SiO_2, atm. press., 2-hr. runs

Mole ratio C_2H_5OH/ CH_3CHO	Mole fraction[a] C_2H_5OH	Mole fraction[a] CH_3CHO	Butadiene yield, mole % Per Pass[c]	Butadiene yield, mole % Ultimate[d]	Efficiency, % C_2H_5-OH	Efficiency, % CH_3-CHO
5.1	0.70	0.14	23	47	30	110
3.5	.66	.19	28	61	45	92
3.0	.64	.21	30	65	51	90
2.75	.63	.23	34	66	55	83
2.5	.61	.25	35	69	61	80
2.0	.58	.29	40	64	59	69
1.75	.56	.32	40	65	64	65
1.0	.45	.45	39[b]	60	65	55
0.5	.20	.40	38[b]	51	69	40
0.0	.0	.83	0[b]	0	..	0

[a] Water constituted the remainder of the feed. [b] High acetaldehyde concentration caused rapid carbonization of the catalyst. [c] Per pass yield =

$$\frac{\text{moles } C_4H_6 \times 100}{(\text{moles } C_2H_5OH + \text{moles } CH_3CHO)/2}.$$

[d] Ultimate yield =

$$\frac{\text{moles } C_4H_6 \times 100}{(\text{moles } C_2H_5OH \text{ reacted} + \text{moles } CH_3CHO \text{ reacted})/2}.$$

---

(12) Ostromislensky, *J. Russ. Phys.-Chem. Soc.*, **47**, 1472 (1915).

(13) Lebedev, *et al.*, *J. Gen. Chem.* (*U. S. S. R.*), **31**, 698 (1933); *Syntet Kauchuk*, **4**, 8 (1935).

(14) Lebedev, French Patent 665,917 (1928); British Patent 331,482 (1930); Talalay and Talalay, *Rubber Chem. Tech.*, **15**, 403 (1942); Talalay and Magat, "Synthetic Rubber from Alcohol," Interscience Publ., Inc., New York, N. Y., 1945.

(15) Acetaldehyde efficiency = $\dfrac{\text{moles } C_4H_6 \text{ produced} \times 100}{\text{moles } CH_3CHO \text{ consumed}}$.

increase the per pass yield of butadiene, but where the feed was aqueous acetaldehyde alone (*ca.* 92% acetaldehyde, 8% water), the yield of butadiene was zero, whereas the yields of crotonaldehyde and by-products were 18 and 25%, respectively. The ultimate yield of butadiene passed through a maximum at the ethanol–acetaldehyde ratio of approximately 2.5/1. On the other hand, the ethanol efficiency[16] increased and the acetaldehyde efficiency[15] decreased as the ethanol–acetaldehyde ratio of the feed was decreased. With an ethanol–acetaldehyde feed mole ratio of 5.1/1 (expt. 1, Table I) the acetaldehyde efficiency was 110%. Because of this complication, kinetic calculations were applied only to feed mole ratios in the range 0.5/1 to 3.5/1.

Table II

Rate Constants at Atmospheric Pressure and 350°

2% Ta_2O_5–98% SiO_2, 8-hr. runs

Mole fraction CH_3CHO In feed	In product	Mole fraction C_2H_5OH In feed	In product	C. T.[a] sec.	C_4H_6 mole fraction	K_1	K_2
0.214	0.056	0.643	0.384	4.5	0.103	0.319	0.252
.214	.031	.643	.343	6.7	.113	.320	.253
.223	.096	.615	.440	2.7	.085	.332	.262
.223	.082	.615	.417	3.4	.096	.317	.250
.223	.060	.615	.382	4.5	.107	.322	.254
.223[b]	.036	.615	.298	6.6	.132	.312	.246
.223	.010	.615	.280	10.6	.138	.334	.264
.247	.037	.616	.310	6.6	.136	.322	.254
.288	.039	.576	.211	6.6	.146	.334	.264
.317[c]	.100	.554	.320	3.8	.107	.313	.247
.400[c]	.088	.200	.023	4.9	.106	.313	.247
.445	.170	.445	.196	2.8	.117	.328	.259
					Av,	.322	.254

[a] C. T. = contact time in seconds, assuming ideal gas laws. [b] Average of 17 expts. [c] 3-hr. expts.

Rate Data for Atmospheric Operation.—The data in Tables II (350°) and III (232–403°) did not support the assumption of a bimolecular reaction between ethanol and acetaldehyde (mechanism A); they fitted a rate equation

$$dx/dt = K_1(a - x)^2 + K_2\,(a - x)$$

$$K_2 = \frac{1}{t}\ln\left[\left(\frac{a}{a - x}\right)\left(\frac{a - x + K_2/K_1}{a + K_2/K_1}\right)\right]$$

where a = initial mole fraction of acetaldehyde, x = mole fraction of acetaldehyde reacted, K_1 = rate constant of acetaldehyde condensation and K_2 = rate constant of side reactions. The expression was solved by simultaneous equations, or by trial and error, depending upon the amount of experimental data. The scattering of the calculated K values due to the ±3° variation of the reaction temperature was ±4%. This was the principal source of error. The scattering due to analytical uncertainty was ±2%.

The apparent activation energies derived from the plots of ln K_1 and ln K_2 against reciprocal temperature were 24 kcal. and 8.5 kcal., respectively. Both plots deviated from linearity at the higher temperatures, especially that of ln K_2. This was

Table III

Rate Constants at Atmospheric Pressure and Various Temperatures

2% Ta_2O_5–98% SiO_2, 8-hr. runs

T, °C.	Mole fraction CH_3CHO In feed	In product	Mole fraction C_2H_5OH In feed	In product	C. T., sec.	C_4H_6 mole fraction	K_1	K_2
232	0.445	0.280	0.445	0.283	8.4	0.089	0.0035	0.054
300	.214	.088	.643	.524	5.0	.041	.057	.170
300	.214	.058	.643	.468	7.5	.056	.056	.167
300	.223	.063	.615	.396	7.4	.078	.055	.164
300	.288	.077	.576	.330	7.4	.090	.056	.169
							.056	.168 (av.)
325	.214	.070	.643	.422	4.7	.089	.141	.219
325	.214	.045	.643	.397	7.0	.091	.139	.216
325	.223	.050	.615	.352	7.0	.102	.129	.200
325	.288	.055	.576	.274	6.9	.122	.142	.220
325	.469	.160	.435	.192	4.3	.097	.136	.211
							.137	.213 (av).
375	.214	.029(0.041)[a]	.643	.242	6.3	.126	.650	.260
375	.223	.030(.033)[a]	.615	.239	6.3	.138	.648	.259
375	.288	.032(.037)[a]	.576	.183	6.2	.155	.697	.279
							.665	.266 (av.)
400	.214	.022(.031)[a]	.643	.092	6.0	.144	1.20	.287
403	.223	.022(.032)[a]	.615	.179	6.0	.141	1.22	.292
397	.288	.023(.036)[a]	.576	.133	6.0	.162	1.28	.306
							1.23	.295 (av.)

[a] Final acetaldehyde concentrations were corrected for acetaldehyde resulting from butene formation in excess of that formed at 350° (uncorrected values in parentheses).

---

[16] $\dfrac{\text{Moles } C_4H_6 \text{ produced} \times 100}{\text{Moles } C_2H_5OH \text{ consumed}}$.

attributed to the formation of acetaldehyde by reactions non-productive of butadiene (*e. g.*, reactions N—R) which decreased the apparent consumption of acetaldehyde.

No satisfactory kinetic equation was derived to fit the experimental data on the rate of butadiene production as a function of ethanol consumption.

Rate Data for Operation at 4–30 Atmospheres.—The rate data in Table IV supported the assumption that the rate of acetaldehyde consumption was directly proportional to the acetaldehyde concentration and inversely proportional to that of the ethanol according to the general theory of Langmuir[17]

$$\frac{-\mathrm{d}Pa}{\mathrm{d}t} = K_{\mathrm{p}}\frac{Pa}{Pe}$$

$$K_{\mathrm{p}} = \frac{1}{t}\left[(Pa_0 - Pe_0)\ln\frac{Pa}{Pa_0} + Pa_0 - Pa\right]$$

where t = contact time in seconds and Pa and Pe = partial pressures of acetaldehyde and ethanol, respectively, subscript 0 denoting the initial state. For convenience in integration it was assumed that $Pe = Pa - Pa_0 + Pe_0$; although incorrect, the resultant deviation in K_{p} apparently was not serious.

TABLE IV

RATE CONSTANTS FOR OPERATION AT 4–30 ATMOSPHERES AT 325°

2% Ta_2O_5–98% SiO_2, 3/1 ethanol–acetaldehyde feed ratio, 8-hr. runs

Total pressure, atm.	Pa_0	Pe_0	Pa	Pe	C. T., sec.	P_b[a]	K_p
1.0	0.214	0.643	0.045	0.397	7.0	0.091	0.120
4.4[b]	.748	2.39	.327	1.83	8.4	.264	.224
4.5	.960	2.89	.648	2.47	7.7	.183	.140
4.6	.985	2.96	.510	2.36	12.7	.276	.141
7.8	1.67	5.01	1.45	4.71	4.4	.131	.156
7.8	1.67	5.01	1.25	4.40	8.5	.340	.160
7.9	1.69	5.08	1.04	4.23	17.0	.385	.133
14.2	3.04	9.13	2.47	8.20	10.9	.352	.168
28.2	6.03	18.1	5.30	16.9	16.7	.474	.138
30.0	6.42	19.3	5.97	18.7	8.7	.255	.161
							.150 (av.)

[a] P_b = partial pressure of butadiene. [b] Expt. made at 340°.

The physical significance of the above differential equation can be visualized in various ways. For example, the slow reaction may be the rate of diffusion of acetaldehyde to the chemisorbed ethanol on the catalyst surface or to the relatively small fraction of the catalyst surface which is not occupied by ethanol. It is, however, unexpected that such a small increase in pressure as three atmospheres should change the order of the reaction.

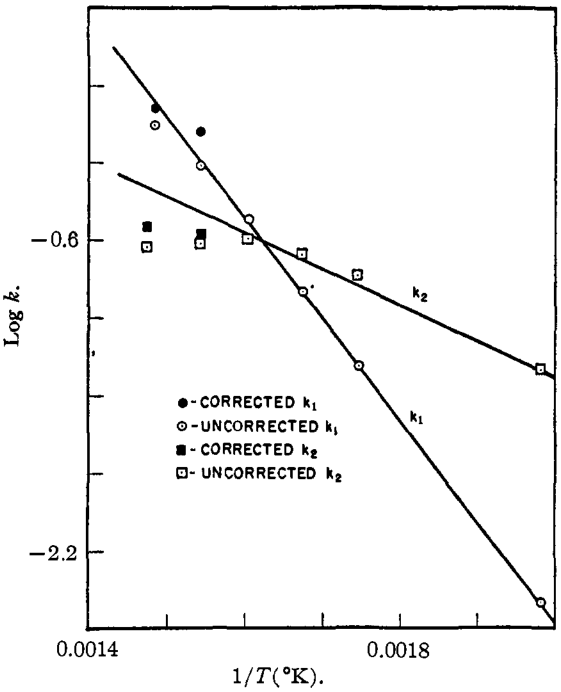


Fig. 1.—Relation between rates of reaction and temperature.

Equilibrium Constants.—From data available in 1943 at the beginning of this study, the equilibrium constant[18] for the formation of butadiene from ethanol–acetaldehyde at 350° was calculated to be 3.55 × 10^5. Using this constant and the experimentally determined K_1 constant, the equilibrium mole fraction of acetaldehyde was calculated to be 5 × 10^{-4} for 2.75/1 ethanol–acetaldehyde feed. Extrapolation of rate data showed that this equilibrium concentration of acetaldehyde would be reached in twenty-two seconds contact time (about 10 times the half-reaction time); at this equilibrium concentration of acetaldehyde a 40% per pass yield of butadiene would be expected. Actually, the yield at this prolonged contact time (eight-hour expt.) was only 30% and the catalyst was excessively carbonized.

Although the per pass yield is presumably not subject to much further improvement, it is, however, possible to increase the ultimate yield by operating in such manner (by multi-addition of acetaldehyde) that the optimal high ethanol–acetaldehyde ratio is approximated throughout the reaction zone.[19]

Efficiency of Acetaldehyde, Crotonaldehyde and Acetaldol[12,20] in Ethanol Feed

Ethanol feeds containing acetaldehyde and the two C_4-aldehydes (acetaldol and crotonaldehyde) were compared on an equivalent basis (3 moles of ethanol per mole of acetaldehyde or 0.5 mole of C_4-aldehyde) at 350° and 0.4 l. h. s. v. The per pass mole yields of butadiene per C_4-aldehyde equivalent were 1.2, 1.2 and 1.8, respectively; the 1.8 mole yield corresponded to 90% of the theoretical. Thus, crotonaldehyde was considerably more ef-

---

[17] Langmuir, *Trans. Farad. Soc.*, **17**, 621 (1922).

[18] Private communication, A. V. Cowan, Koppers Company, Inc.

[19] Kampmeyer and Stahly, *Ind. Eng. Chem.*, **41**, 550 (1949).

[20] Maximoff, U. S. Patent 1,682,919 (1928).

TABLE V

PERFORMANCE OF ETHANOL–CROTONALDEHYDE AND ETHANOL–ACETALDEHYDE FEEDS

0.4 l. h. s. v., 2% Ta_2O_5–98% SiO_2, 4-hr. expts., atm. press

	Ethanol–crotonaldehyde feed								Ethanol–acetaldehyde feed			
Temperature, °C.	350	350	350	325	325	325	300	275	350	325	300	230
Feed mole ratio (alc./ald.)	2/1	3/1	6/1	3/1	6/1	8/1	6/1	6/1	3/1	3/1	3/1	1/1
Moles C_4H_6 produced per mole equivalent C_4-aldehyde	0.7	1.4	1.8	1.0	1.2	1.5	1.0	0.7	1.2	1.0	0.6	0.4
C_4H_6 % yield based on total feed	36[a]	56[a]	48[a]	40[a]	30[a]	32[a]	24[a]	17[a]	30[b]	24[b]	14[b]	22[b]

[a] $\frac{\text{Moles butadiene} \times 100}{(\text{Moles ethanol})/2 + \text{moles } C_4\text{-aldehyde}}$. [b] $\frac{\text{Moles butadiene} \times 100}{(\text{Moles ethanol})/2 + (\text{moles acetaldehyde})/2}$.

fective than acetaldol, the latter being merely equivalent to acetaldehyde. Evidently, acetaldol was reversed to acetaldehyde and not dehydrated to crotonaldehyde. Table V presents additional data supporting the hypothesis that the formation of crotonaldehyde is a rate determining reaction; *i. e.*, the yield of butadiene from ethanol–crotonaldehyde was considerably greater than that from ethanol–acetaldehyde. Incidentally, the formation of butadiene from ethanol–acetaldehyde was appreciable at 230°, *i. e.*, 120° lower than the commercially employed temperature.

Functions of Silica and Tantala Components of Catalyst

Condensation of Acetaldehyde.—Unpromoted silica was more effective than tantala-promoted silica for the above condensation. Silica gel at 280° and 0.4 l.h.s.v. converted 22 mole % of the acetaldehyde to crotonaldehyde and 13 mole % to by-products, whereas 2% Ta_2O_5–98% SiO_2 under the same conditions converted 12 mole % to crotonaldehyde and 15 mole % to by-products. Silica gel at 350° and 0.4 l.h.s.v. converted 26 mole % of the acetaldehyde to crotonaldehyde and 16 mole % to by-products, whereas 2% Ta_2O_5–98% SiO_2 under the same conditions converted 18 mole % to crotonaldehyde and 25 mole % to by-products.

Catalysis of Ethanol Mixtures of Acetaldehyde, Crotonaldehyde and Crotyl Alcohol over Unpromoted SiO_2 and 2% Ta_2O_5–98% SiO_2.—Unpromoted silica was more effective for the dehydration of crotyl alcohol to butadiene, but promoted silica was more effective for feeds requiring deoxygenation, *e. g.*, ethanol–acetaldehyde, ethanol–crotonaldehyde and crotonaldehyde–crotyl alcohol feeds (Table VI). The different conclusion of Toussaint, Dunn and Jackson[3] was possibly due to the use of a different type of silica gel. Crotyl alcohol has been proposed[21] as source material for butadiene and as an intermediate in the ethanol process for butadiene.[22] When crotyl alcohol was processed at 350° in runs longer than one hour the catalyst was excessively carbonized, and when the temperature was raised to 400°, the production of by-product gas increased at the expense of butadiene.

TABLE VI

BUTADIENE PRODUCTION OVER SiO_2 AND 2% Ta_2O_5–98% SiO_2 AT 350° (one-hour runs)

Feed	Catalyst	l. h. s. v.	Mole % C_4H_6 based on total feed
Ethanol–crotonaldehyde (6/1)	SiO_2	1	8
Ethanol–crotonaldehyde (6/1)	2% Ta_2O_5–98% SiO_2	1	48[a]
Ethanol–acetaldehyde (3/1)	SiO_2	1	3
Ethanol–acetaldehyde (3/1)	2% Ta_2O_5–98% SiO_2	1	20
Crotyl alcohol	SiO_2	1	41
Crotyl alcohol	2% Ta_2O_5–98% SiO_2	1	32
Crotyl alcohol	SiO_2	0.4	75
Crotyl alcohol	2% Ta_2O_5–98% SiO_2	0.4	50

[a] Forty-eight mole % yield corresponds to the formation of 1.92 moles of butadiene per mole of crotonaldehyde fed (96% of the theoretical yield).

Catalysis by SiO_2 Admixed with 2% Ta_2O_5–98% SiO_2.—Since unpromoted silica gel was more effective than tantala-promoted silica for the dehydration of crotyl alcohol, it follows that, if the dehydration of crotyl alcohol be a rate determining step, a mixture of unpromoted and promoted catalysts should be more effective than either alone. Two tests were made in which 2.75/1 ethanol–acetaldehyde feed was passed at 350° over equal volumes of (1) promoted catalyst, and (2) a 50/50 mixture of unpromoted and promoted catalysts. The per pass yields of butadiene over the promoted catalyst and over the unpromoted–promoted mixture at 0.4 l.h.s.v. were 35 and 25%, respectively; at 0.8 l.h.s.v. over the promoted catalyst, which was the space velocity with respect to the promoted component of the mixture of catalysts, the yield of butadiene was 25%. Therefore the dehydration of crotyl alcohol was not a rate determining step.

Deoxygenation of Crotonaldehyde by Ethanol, Isopropyl Alcohol and Crotyl Alcohol over SiO_2

---

[21] Kyriakides, THIS JOURNAL, **36**, 986 (1914); Prevost, *Ann. Chim.*, [10] **10**, 152, 407 (1928).

[22] Rigamonti and Cardillo, *Ann. chim. applicata*, **37**, 347 (1947); Natta and Rigamonti, *Chemica e Industria*, **29**, 195 (1947).

and 2% Ta_2O_5–98% SiO_2.—The function of ethanol was to deoxygenate crotonaldehyde, but other alcohols could also serve. For example, as shown in Table VII, crotonaldehyde–isopropanol produced butadiene although with considerable C_5- and C_3-by-products. A 60% yield of butadiene per pass was produced by crotonaldehyde–crotyl alcohol over Ta_2O_5–SiO_2, but the yield was considerably less over unpromoted silica, which is confirmatory evidence for the deoxygenating function of the tantala promoter.

TABLE VII

DEOXYGENATION OF CROTONALDEHYDE BY ETHANOL, ISOPROPYL ALCOHOL, AND CROTYL ALCOHOL OVER SiO_2 AND 2% Ta_2O_5–98% SiO_2

350°, 0.6 l. h. s. v., 1-hr. expts.

	Moles of C_4H_6 produced per mole of		
2% Ta_2O_5–98% SiO_2	Crotonaldehyde	Crotyl alcohol	C_4-equivalent
Ethanol–crotonaldehyde (6/1)	1.6	..	0.40
Isopropyl alcohol–crotonaldehyde (6/1)	0.6	..	.15
Crotyl alcohol–crotonaldehyde (6/1)	3.6	0.60	.51
Crotyl alcohol	...	0.43[a]	.43
SiO_2			
Ethanol–crotonaldehyde (6/1)	0.6	..	.15
Isopropyl alcohol–crotonaldehyde (6/1)	0.2	..	.05
Crotyl alcohol–crotonaldehyde (6/1)	2.1	0.35[b]	.30
Crotyl alcohol	...	0.65[a]	.65

[a] Catalyst was rapidly carbonized; molal yields in 4-hour runs over promoted and unpromoted catalysts, respectively, were 0.40 and 0.25. [b] The predicted yield on the basis of the performance of crotyl alcohol alone was about 0.55 mole.

Generation *in Situ* of Ethanol and Acetaldehyde (or Crotonaldehyde).—It was not surprising that various systems (Table VIII) capable of generating the above reactants produced butadiene at rates roughly inversely proportional to the number and difficulty of the generative steps. For example, in unit time, acetal gave less butadiene than acetaldehyde, ethylene oxide less than acetal, and ethylene glycol less than ethylene oxide. Butadiene production from ethyl acetate–water–acetaldehyde has commercial significance because ethyl acetate is a by-product of the commercial process.[23]

TABLE VIII

BUTADIENE PRODUCTION FROM VARIOUS FEEDS

350°, 0.4 l. h. s. v., 2% Ta_2O_5–98% SiO_2

Feed	Feed mole ratio	Per C_4 equivalent other than ethanol	Per total C_4-equivalent
Ethanol	...	0.0	0.02
Ethanol–acetaldehyde	3/1	1.20	.30
Ethanol–acetal	3/1	1.12	.28
Ethanol–paraldehyde	3/1	1.12	.28
Ethanol–ethylene oxide	3/1	0.80	.20
Ethanol–ethylene glycol	3/1	0.08	.02
Ethanol–crotonaldehyde	6/1	1.80	.45
Ethanol–acetaldol	6/1	1.20	.30
Ethanol–methyl vinyl ketone	3/1	0.60	.24
Ethanol–diacetyl	4/1	0.51	.17
Ethanol–butyraldehyde	3/1	0.22	.09
Ethanol–acetone	3/1	1.00	.25
Isopropyl alcohol–acetaldehyde	3/1	0.60	.12
1,3-Butanediol	...	0.12	.12
Ethanol–butadiene monoxide	2/1	0.52	.26
Ethanol–butadiene monoxide	6/1	1.48	.37
Ethanol–dioxolane	6/1	0.84	.12
Methyl dioxolane	...	0.10	.10
Ethyl acetate–water–acetaldehyde	3/1.5/1	0.80	.20

Miscellaneous Mechanisms

Butanol, Butyraldehyde and Butanediols as Intermediates.—*n*-Butanol (mechanism G) did not produce butadiene under the conditions of the present process, which eliminated the possibility of *n*-butyraldehyde as intermediate (mechanism G_3). Ethanol–butyraldehyde gave a 9% per pass yield (Table VIII), but this butadiene probably did not come from butyraldehyde but from acetaldehyde formed in the reduction of butyraldehyde by ethanol; by-products were *n*-butanol and butanes (mole ratio 5/1). 1,3-Butanediol, proposed by Ostromislensky[12] as intermediate, gave a 12% per pass yield of butadiene, whereas ethanol–acetaldehyde gave a 30% yield; 1,2- and 2,3- butanediols gave no more than traces of butadiene.

Vinyl Ether–Ethylene, Acetaldehyde–Ethylene and Acetaldehyde–Acetylene.—These feed mixtures (mechanisms H_2 and I)[24] were processed over a variety of catalysts, including aluminum and 2% Ta_2O_5–98% SiO_2, under the conditions of the ethanol–butadiene process. The yield of butadiene was negligible in all cases. The addition of 4% of acetylene to the commercial feed (ethanol–acetaldehyde) showed no benefit; the acetylene was recovered unchanged.

Additional Non-operative Feeds.—Table IX lists 28 feeds from which only traces of butadiene were obtained upon processing over 2% Ta_2O_5–98% SiO_2 under the commercial conditions of the American ethanol–butadiene process. The majority of these feeds contained intermediates of mechanisms proposed by various investigators[11]; others were mixtures of acetaldehyde (or ethylene oxide) with possible hydrogen donors. Doubtless certain of these feeds would produce butadiene with the proper catalysts and conditions, but the

---

[23] Stahly, U. S. Patent 2,439,587 (1948); Stahly, Jones and Corson, *Ind. Eng. Chem.*, **40**, 2301 (1948).

[24] Miller, U. S. Patent 2,377,025 (1945).

present interest was the mechanism of the specific ethanol–butadiene process as operated.

TABLE IX

NON-OPERATIVE FEEDS

1,4-Dioxane
Ethanol-1,4-dioxane
Butadiene monoxide
Tetrahydrofuran
Thiophene
Ethanol–thiophene
Dioxolane
2-Methyl-1,3-dioxolane
Ethanol-2-methyl-1,3-dioxolane
Ethanol–glyoxal hydrate
Ethanol–ethyl vinyl ether
Pyrrole
1,2-Butanediol
Ethanol–water–pyrrole
Ethylene–ethyl vinyl ether
Ethylene–acetal
Ethanol–water–diethyl ether
Ethanol–water–ethyl acetate
Ethanol–water–ethylene
Acetaldehyde
Acetaldehyde–water–diethyl ether
Cyclohexanol–acetaldehyde
Cyclohexene
Cyclohexene–acetaldehyde
Ethyltetralin–acetaldehyde
Ethyltetralin–ethylene oxide
2,3-Butanediol (*levo* and *meso* with and without ethanol)

Acknowledgment.—Thanks are expressed to J. Cohen and B. J. Steenbergen for assistance in the experimental work; to G. C. Akerlof, J. R. Bowman and P. H. Emmett for valuable comments; and to L. H. Cretcher and E. R. Weidlein for friendly encouragement.

Summary

1. The rate controlling process in the second step of the ethanol–butadiene process at atmospheric pressure is a second order condensation of acetaldehyde to crotonaldehyde, whereas at pressures of 4–30 atmospheres the rate of consumption of acetaldehyde is of first order.

2. The final reaction which produces butadiene is the deoxygenation of crotonaldehyde by ethanol.

3. A mixture of crotyl alcohol with a minor amount of crotonaldehyde is ideal for the production of butadiene under the conditions of the ethanol–butadiene process (60 mole % yield per pass).

4. Feed mixtures capable of producing acetaldehyde (or crotonaldehyde) *in situ* produce butadiene when processed over Ta_2O_5–SiO_2 catalyst.

5. The primary function of the silica component of the commercial catalyst is to catalyze the condensation of acetaldehyde, whereas the function of the tantala promoter is to catalyze the deoxygenation of crotonaldehyde by ethanol.

6. Numerous mechanisms proposed by various investigators were demonstrated to be inoperative under the conditions of the second step of the American ethanol–butadiene process.

PITTSBURGH, PA. RECEIVED JUNE 30, 1948

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF TEMPLE UNIVERSITY]

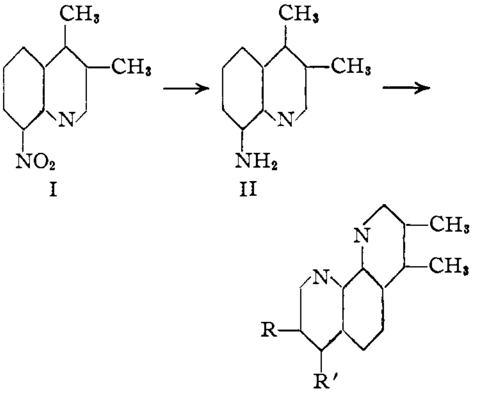
Substituted 1,10-Phenanthrolines. III.[1,2] Polymethyl Phenanthrolines Related to 3,4-Dimethyl-1,10-phenanthroline

BY FRANCIS H. CASE

The use of 1-hydroxy-2-methyl-3-butanone, $CH_3COCH(CH_3)CH_2OH$, as a reactant in the Skraup synthesis has been limited[3,4] to the synthesis of 3,4-dimethylquinoline. In this Laboratory a series of polymethyl-1,10-phenanthrolines has been prepared by the use of the above keto alcohol with the object of furnishing derivatives which in the form of their ferrous complexes would be likely to have a low oxidation potential.

The action of *o*-nitroaniline and 1-hydroxy-2-methyl-3-butanone under Skraup conditions yielded 3,4-dimethyl-8-nitroquinoline I (see diagram). The corresponding aminoquinoline II under Skraup conditions yielded 3,4-dimethyl-1,10-phenanthroline III (with glycerol); 3,4,7,8-tetramethyl-1,10-phenanthroline IV (with 1-hydroxy-2-methyl-3-butanone); 3,4,8-trimethyl-1,10-phenanthroline V (with methylacrolein diacetate (2-methyl-2-propene-1,1-diol diacetate); and 3,4,7-trimethyl-1,10-phenanthroline VI (with methyl vinyl ketone).

The action of 2-nitro-4-methylaniline and 1-hydroxy-2-methyl-3-butanone yielded 3,4,6-trimethyl-8-nitroquinoline VII. The corresponding amine VIII yielded on reaction with glycerol, 3,4,6-trimethyl-1,10-phenanthroline IX; with methylacrolein diacetate, 3,4,6,8-tetramethyl-1,10-phenanthroline X; and with methyl vinyl



$\text{II} + \text{G} \longrightarrow \text{III}$ R and R′ = H
$\text{II} + \text{MB} \longrightarrow \text{IV}$ R and R′ = CH_3
$\text{II} + \text{MAD} \longrightarrow \text{V}$ R = CH_3, R′ = H
$\text{II} + \text{MVK} \longrightarrow \text{VI}$ R = H, R′ = CH_3

---

[1] For other papers in this series see Case, THIS JOURNAL, **70**, 3994 (1948), and **71**, 821 (1949).

[2] This work was supported by a Grant from the Committee on Research and Publications of Temple University.

[3] Prill and Walter, United States Patent, 1,806,563 (1931).

[4] Manske, Marion and Leger, *Can. J. Res.*, **20B**, 133 (1942).